DFT, plane waves, and the PAW method

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A system of N electrons

$$\hat{H}\Psi(\mathbf{r}_1, ..., \mathbf{r}_N) = E\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$$

$$\left(-\frac{1}{2}\sum_i \Delta_i + \sum_i V(\mathbf{r}_i) + \sum_{i \neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right)\Psi(\mathbf{r}_1, ..., \mathbf{r}_N) = E\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$$

Many-body WF storage requirements are prohibitive

$$(\#\text{grid points})^N$$

Map onto "one-electron" theory

$$\Psi(\mathbf{r}_1, ..., \mathbf{r}_N) \rightarrow \{\psi_1(\mathbf{r}), \psi_2(\mathbf{r}), ..., \psi_N(\mathbf{r})\}$$

such as Hohenberg-Kohn-Sham density functional theory

Do not need $\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$, just the density $\rho(\mathbf{r})$:

$$E[\rho] = T_s[\{\psi_i[\rho]\}] + E_H[\rho] + E_{\mathrm{xc}}[\rho] + E_Z[\rho] + U[Z]$$

$$\Psi(\mathbf{r}_1, ..., \mathbf{r}_N) = \prod_i^N \psi_i(\mathbf{r}_i) \qquad \rho(\mathbf{r}) = \sum_i^N |\psi_i(\mathbf{r})|^2 \qquad E_H[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

One-electron Kohn-Sham equations

$$\left(-\frac{1}{2}\Delta + V_Z(\mathbf{r}) + V_H[\rho](\mathbf{r}) + V_{\mathrm{xc}}[\rho](\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

Hartree   Exchange-Correlation

$$V_H[\rho](\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \qquad E_{\mathrm{xc}}[\rho] = ??? \qquad V_{\mathrm{xc}}[\rho](\mathbf{r}) = ???$$

Per definition: $E_{\mathrm{xc}} = E - T_s - E_H - E_{\mathrm{ext}}$

In practice: Exchange-Correlation functionals are modelled on the uniform electron gas (Monte Carlo calculations): e.g., local density approximation (LDA).

- Translational invariance implies the existence of a good quantum number, usually called the Bloch wave vector $\mathbf{k}$. All electronic states can be indexed by this quantum number

$$|\Psi_{\mathbf{k}}\rangle$$

- In a one-electron theory, one can introduce a second index, corresponding to the one-electron band $\mathbf{n}$,
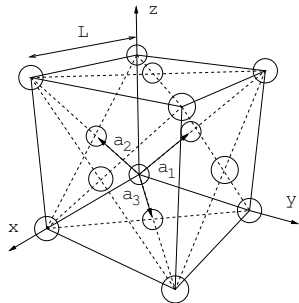
$$|\psi_{n\mathbf{k}}\rangle$$

- The Bloch theorem states that the one-electron wavefunctions obey the equation:
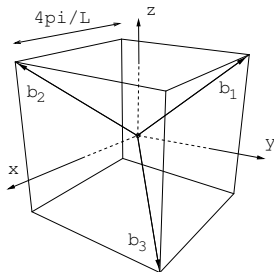
$$\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = \psi_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\mathbf{R}}$$

where $\mathbf{R}$ is any translational vector leaving the Hamiltonian invariant.
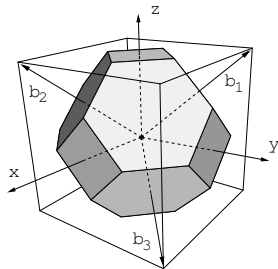
- $\mathbf{k}$ is usually constrained to lie within the first Brillouin zone in reciprocal space.

A   B   C

$$\mathbf{b}_1 = \frac{2\pi}{\Omega}\mathbf{a}_2 \times \mathbf{a}_3 \quad \mathbf{b}_2 = \frac{2\pi}{\Omega}\mathbf{a}_3 \times \mathbf{a}_1 \quad \mathbf{b}_3 = \frac{2\pi}{\Omega}\mathbf{a}_1 \times \mathbf{a}_2$$

$$\Omega = \mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3 \qquad \mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$$

- The evaluation of many key quantities, e.g. charge density, density-of-states, and total energy) requires integration over the first BZ. The charge density $\rho(\mathbf{r})$, for instance, is given by

$$\rho(\mathbf{r}) = \frac{1}{\Omega_{\mathrm{BZ}}} \sum_n \int_{\mathrm{BZ}} f_{n\mathbf{k}} |\psi_{n\mathbf{k}}(\mathbf{r})|^2 d\mathbf{k}$$

- $f_{n\mathbf{k}}$ are the occupation numbers, i.e., the number of electrons that occupy state $n\mathbf{k}$.

- Exploiting the fact that the wave functions at $\mathbf{k}$-points that are close together will be almost identical, one may approximate the integration over $\mathbf{k}$ by a weighted sum over a discrete set of points

$$\rho(\mathbf{r}) = \sum_n \sum_{\mathbf{k}} w_{\mathbf{k}} f_{n\mathbf{k}} |\psi_{n\mathbf{k}}(\mathbf{r})|^2 d\mathbf{k},$$

where the weights $w_{\mathbf{k}}$ sum up to one.

The intractable task of determining $\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$ (for $N \sim 10^{23}$) has been reduced to calculating $\psi_{n\mathbf{k}}(\mathbf{r})$ at a discrete set of points $\{\mathbf{k}\}$ in the first BZ, for a number of bands that is of the order of the number of electrons *per unit cell*.
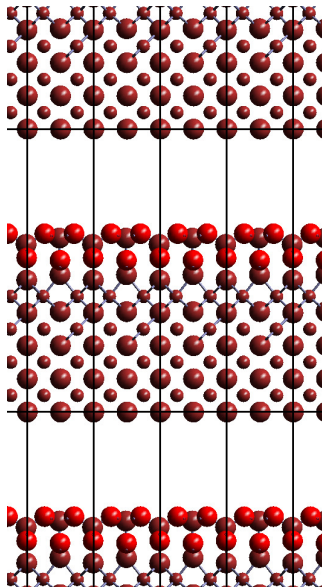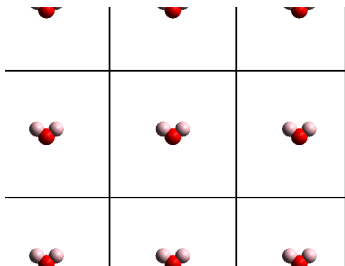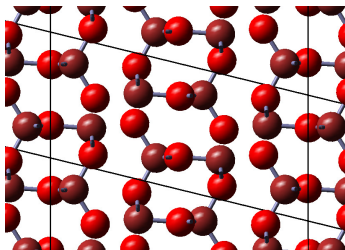
- The total energy

$$E[\rho, \{\mathbf{R}, Z\}] = T_s[\{\psi_{n\mathbf{k}}[\rho]\}] + E_H[\rho, \{\mathbf{R}, Z\}] + E_{\mathrm{xc}}[\rho] + U(\{\mathbf{R}, Z\})$$

- The kinetic energy

$$T_s[\{\psi_{n\mathbf{k}}[\rho]\}] = \sum_n \sum_{\mathbf{k}} w_{\mathbf{k}} f_{n\mathbf{k}} \langle \psi_{n\mathbf{k}} | -\frac{1}{2}\Delta | \psi_{n\mathbf{k}} \rangle$$

- The Hartree energy

$$E_{\mathrm{H}}[\rho, \{\mathbf{R}, Z\}] = \frac{1}{2} \iint \frac{\rho_{eZ}(\mathbf{r})\rho_{eZ}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r}$$

  where $\rho_{eZ}(\mathbf{r}) = \rho(\mathbf{r}) + \sum_i Z_i \delta(\mathbf{r} - \mathbf{R}_i)$

- The electronic charge density

$$\rho(\mathbf{r}) = \sum_n \sum_{\mathbf{k}} w_{\mathbf{k}} f_{n\mathbf{k}} |\psi_{n\mathbf{k}}(\mathbf{r})|^2 d\mathbf{k},$$

- The Kohn-Sham equations

$$\left(-\frac{1}{2}\Delta + V_H[\rho_{eZ}](\mathbf{r}) + V_{\mathrm{xc}}[\rho](\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) = \epsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

- The Hartree potential

$$V_H[\rho_{eZ}](\mathbf{r}) = \int \frac{\rho_{eZ}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

- Introduce the cell periodic part $u_{n\mathbf{k}}$ of the wavefunctions

$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\mathbf{r}}$$

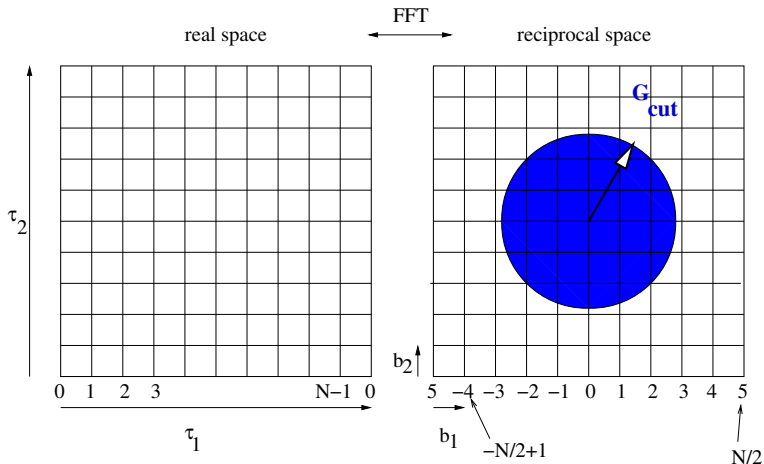 with $u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$.

- All cell periodic functions are now written as a sum of plane waves

$$u_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega^{1/2}} \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}}e^{i\mathbf{G}\mathbf{r}} \quad \psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega^{1/2}} \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}}e^{i(\mathbf{G}+\mathbf{k})\mathbf{r}}$$
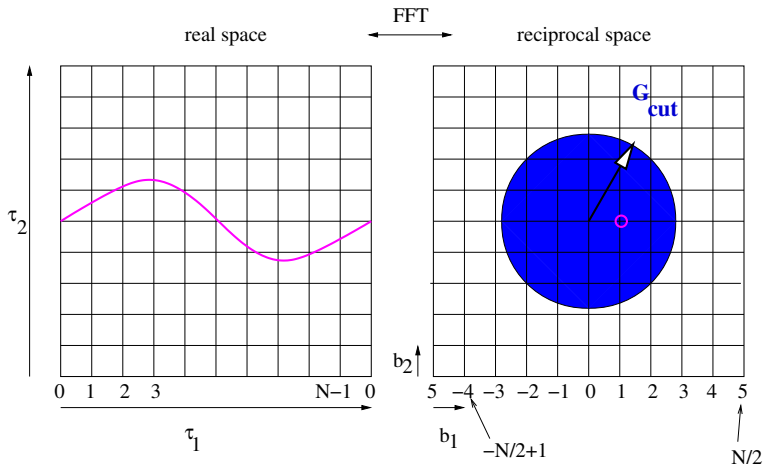
$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}}e^{i\mathbf{G}\mathbf{r}} \qquad V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}}e^{i\mathbf{G}\mathbf{r}}$$

- In practice only those plane waves $|\mathbf{G} + \mathbf{k}|$ are included for which

$$\frac{1}{2}|\mathbf{G} + \mathbf{k}|^2 < E_{\text{cutoff}}$$

FFT

real space ←——→ reciprocal space

τ_2

G_{cut}

τ_1

b_2

0 1 2 3   N−1 0

5 −4 −3 −2 −1 0 1 2 3 4 5

b_1

−N/2+1

N/2

$x_1 = n_1 / N \; \tau_1$

$g_1 = n_1 \, 2\pi / \tau_1$

$$C_{\mathbf{r}n\mathbf{k}} = \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}} e^{i\mathbf{G}\mathbf{r}} \quad \overset{\text{FFT}}{\longleftrightarrow} \quad C_{\mathbf{G}n\mathbf{k}} = \frac{1}{N_{\text{FFT}}} \sum_{\mathbf{r}} C_{\mathbf{r}n\mathbf{k}} e^{-i\mathbf{G}\mathbf{r}}$$
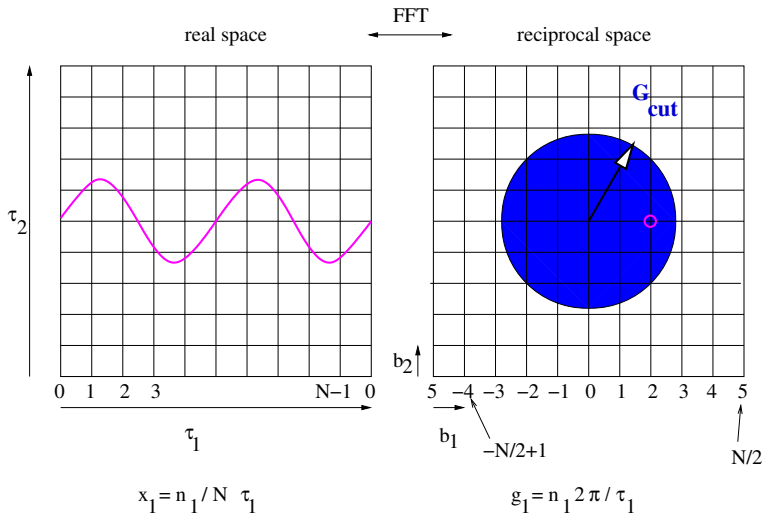
$$C_{\mathbf{r}n\mathbf{k}} = \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}} e^{i\mathbf{G}\mathbf{r}} \quad \xleftrightarrow{\text{FFT}} \quad C_{\mathbf{G}n\mathbf{k}} = \frac{1}{N_{\text{FFT}}} \sum_{\mathbf{r}} C_{\mathbf{r}n\mathbf{k}} e^{-i\mathbf{G}\mathbf{r}}$$
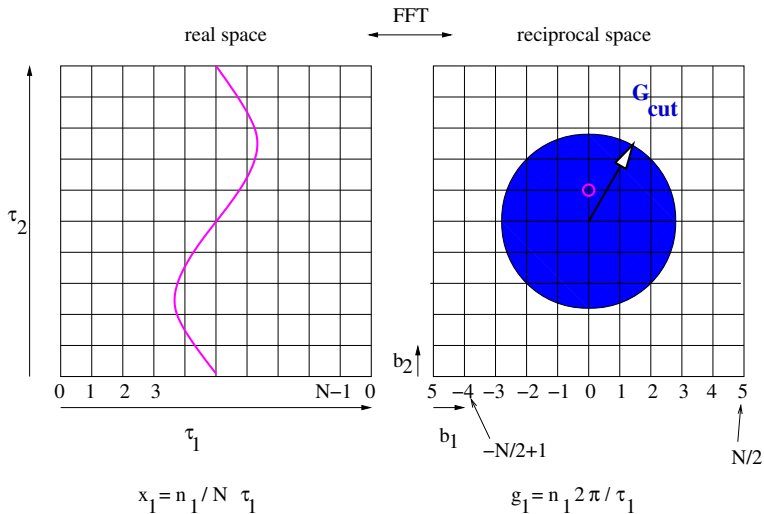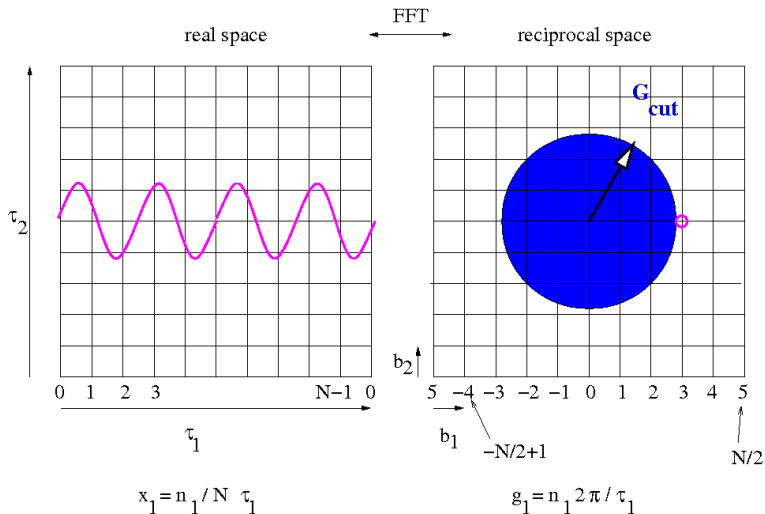
real space $\qquad$ FFT $\qquad$ reciprocal space

$x_1 = n_1 / N \; \tau_1$ $\qquad\qquad\qquad$ $g_1 = n_1 \, 2\pi / \tau_1$

$$C_{\mathbf{r}n\mathbf{k}} = \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}} e^{i\mathbf{G}\mathbf{r}} \quad \overset{\text{FFT}}{\longleftrightarrow} \quad C_{\mathbf{G}n\mathbf{k}} = \frac{1}{N_{\text{FFT}}} \sum_{\mathbf{r}} C_{\mathbf{r}n\mathbf{k}} e^{-i\mathbf{G}\mathbf{r}}$$

FFT

real space $\longleftrightarrow$ reciprocal space

τ_2

$\mathbf{G_{cut}}$

b_2

τ_1

0 1 2 3   N−1 0

5 −4 −3 −2 −1 0 1 2 3 4 5

b_1

−N/2+1

N/2

$$x_1 = n_1 / N \;\; \tau_1$$

$$g_1 = n_1 \, 2\pi / \tau_1$$

$$C_{\mathbf{r}n\mathbf{k}} = \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}} e^{i\mathbf{G}\mathbf{r}} \quad \xleftrightarrow{\text{FFT}} \quad C_{\mathbf{G}n\mathbf{k}} = \frac{1}{N_{\text{FFT}}} \sum_{\mathbf{r}} C_{\mathbf{r}n\mathbf{k}} e^{-i\mathbf{G}\mathbf{r}}$$

FFT

real space

reciprocal space

$\mathbf{G_{cut}}$

τ_2

b_2

0 1 2 3 ... N−1 0

5 −4 −3 −2 −1 0 1 2 3 4 5

b_1

−N/2+1

N/2

τ_1

$x_1 = n_1 / N \ \tau_1$

$g_1 = n_1 \, 2\pi / \tau_1$

$$C_{\mathbf{r}n\mathbf{k}} = \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}} e^{i\mathbf{Gr}} \quad \xleftarrow{\text{FFT}} \quad C_{\mathbf{G}n\mathbf{k}} = \frac{1}{N_{\text{FFT}}} \sum_{\mathbf{r}} C_{\mathbf{r}n\mathbf{k}} e^{-i\mathbf{Gr}}$$

Why use plane waves?

- Historical reason: Many elements exhibit a band-structure that can be interpreted in a free electron picture (metallic s and p elements). Pseudopotential theory was initially developed to cope with these elements (pseudopotential perturbation theory).

- Practical reason: The total energy expressions and the Hamiltonian $\mathbf{H}$ are easy to implement.

- Computational reason: The action $\mathbf{H}|\psi\rangle$ can be efficiently evaluated using FFT's.

Evaluation of $\mathbf{H}|\psi_{n\mathbf{k}}\rangle$

$$\left(-\frac{1}{2}\Delta + V(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r})$$

using the convention

$$\langle\mathbf{r}|\mathbf{G}+\mathbf{k}\rangle = \frac{1}{\Omega^{1/2}}e^{i(\mathbf{G}+\mathbf{k})\mathbf{r}} \rightarrow \langle\mathbf{G}+\mathbf{k}|\psi_{n\mathbf{k}}\rangle = C_{\mathbf{G}n\mathbf{k}}$$
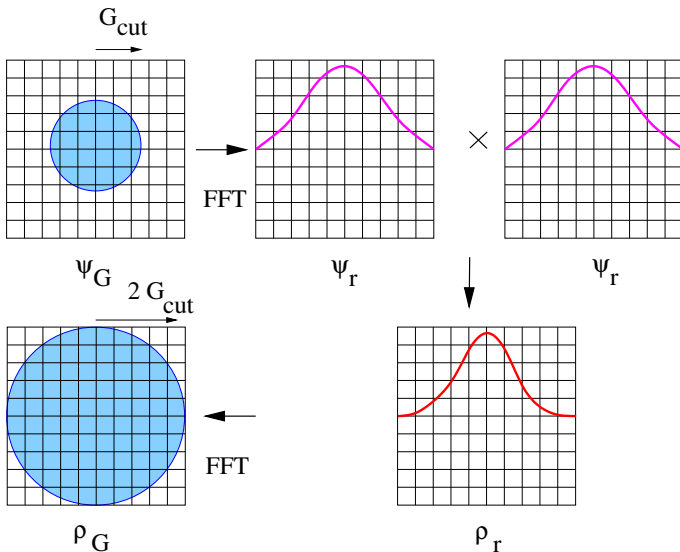
- Kinetic energy:

$$\langle\mathbf{G}+\mathbf{k}| -\frac{1}{2}\Delta|\psi_{n\mathbf{k}}\rangle = \frac{1}{2}|\mathbf{G}+\mathbf{k}|^2 C_{\mathbf{G}n\mathbf{k}} \qquad N_{\mathrm{NPLW}}$$

- Local potential: $V = V_{\mathrm{H}}[\rho] + V_{xc}[\rho] + V_{\mathrm{ext}}$
) Exchange-correlation: easily obtained in real space $V_{xc,\mathbf{r}} = V_{xc}[\rho_\mathbf{r}]$
) FFT to reciprocal space $\{V_{xc,\mathbf{r}}\} \rightarrow \{V_{xc,\mathbf{G}}\}$
) Hartree potential: Poisson equation in reciprocal space $V_{\mathrm{H},\mathbf{G}} = \frac{4\pi}{|\mathbf{G}|^2}\rho_\mathbf{G}$
) add all contributions $V_\mathbf{G} = V_{\mathrm{H},\mathbf{G}} + V_{xc,\mathbf{G}} + V_{\mathrm{ext},\mathbf{G}}$
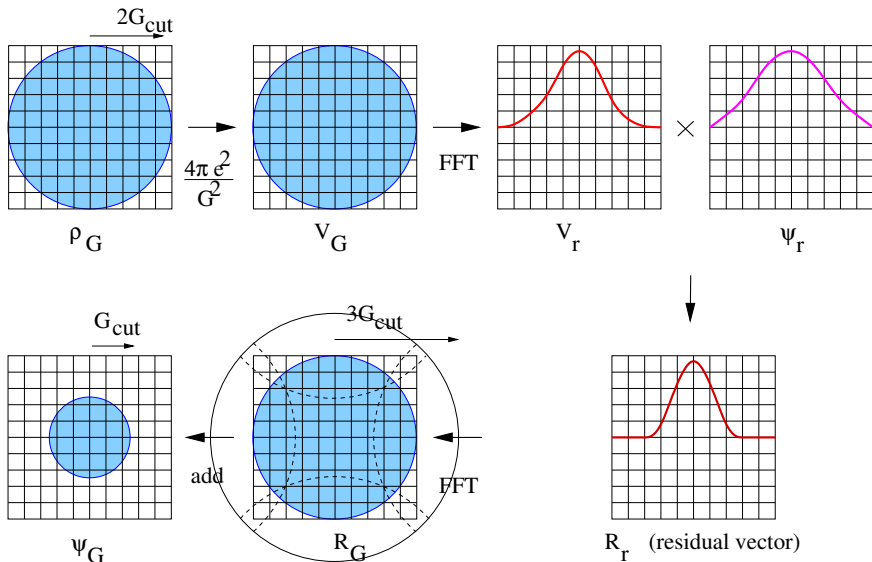) FFT to real space $\{V_\mathbf{G}\} \rightarrow \{V_\mathbf{r}\}$
  The action

$$\langle\mathbf{G}+\mathbf{k}|V|\psi_{n\mathbf{k}}\rangle = \frac{1}{N_{\mathrm{FFT}}}\sum_\mathbf{r} V_\mathbf{r}C_{\mathbf{r}n\mathbf{k}}e^{-i\mathbf{G}\mathbf{r}} \qquad N_{\mathrm{FFT}}\log N_{\mathrm{FFT}}$$

The charge density

The action of the local potential

The PAW method

The number of plane waves needed to describe

- tightly bound (spatially strongly localized) states

- the rapid oscillations (nodal features) of the wave functions near the nucleus

exceeds any practical limit, except maybe for Li and H.

The common solution:

- Introduce the frozen core approximation:
  Core electrons are pre-calculated in an atomic environment and kept frozen in the course of the remaining calculations.

- Use pseudopotentials instead of exact potentials:
) Norm-conserving pseudopotentials
) Ultra-soft pseudopotentials
) The Projector-Augmented-Wave (PAW) method
    [P.E. Blöchl, Phys. Rev. B 50, 17953 (1994)]
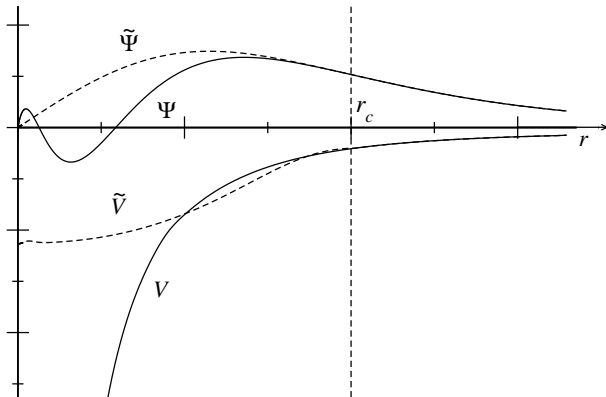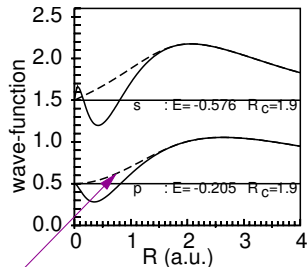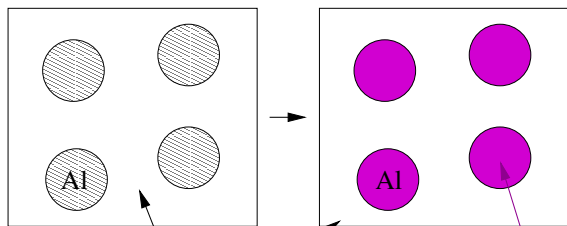
exact potential (interstitial region)   pseudopotential

Al	effective Al atom	PAW Al atom
3p	2p	3p
3s	1s	3s
~~2p~~		
~~2s~~	2p and 1s are	nodal structure
~~1s~~	nodeless !!!!	is retained

$$|\psi_n\rangle = |\widetilde{\psi}_n\rangle + \sum_i (|\phi_i\rangle - |\widetilde{\phi}_i\rangle)\langle\widetilde{p}_i|\widetilde{\psi}_n\rangle$$

- $|\widetilde{\psi}_n\rangle$ is a pseudo wave function expanded in plane waves
- $|\phi_i\rangle$, $|\widetilde{\phi}_i\rangle$, and $|\widetilde{p}_i\rangle$ are atom centered localized functions
- the all-electron partial waves $|\phi_i\rangle$ are obtained as solutions to the radial scalar relativistic Schrödinger equation for the spherical non-spinpolarized atom

$$(-\frac{1}{2}\Delta + v_{\text{eff}})|\phi_i\rangle = \epsilon_i|\phi_i\rangle$$

- a pseudization procedure yields

$$|\phi_i\rangle \rightarrow |\widetilde{\phi}_i\rangle \qquad v_{\text{eff}} \rightarrow \widetilde{v}_{\text{eff}} \qquad \langle\widetilde{p}_i|\widetilde{\phi}_j\rangle = \delta_{ij}$$

- the pseudo partial waves $|\widetilde{\phi}_k\rangle$ obey

$$\left(-\frac{1}{2}\Delta + \widetilde{v}_{\text{eff}} + \sum_{ij} |\widetilde{p}_i\rangle D_{ij}\langle\widetilde{p}_j| \right)|\widetilde{\phi}_k\rangle = \epsilon_k \left(1 + \sum_{ij} |\widetilde{p}_i\rangle Q_{ij}\langle\widetilde{p}_j| \right)|\widetilde{\phi}_k\rangle$$
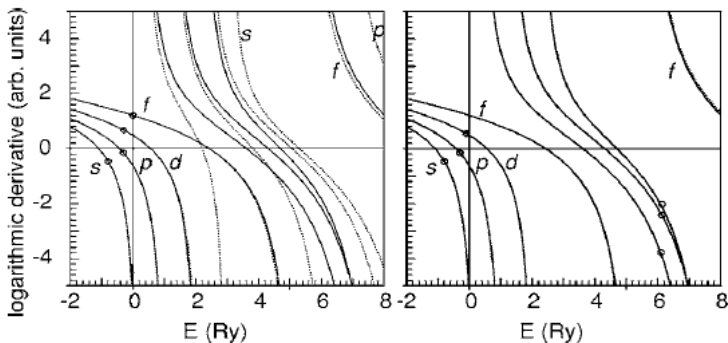
- with the socalled PAW parameters:

$$Q_{ij} = \langle\phi_i|\phi_j\rangle - \langle\widetilde{\phi}_i|\widetilde{\phi}_j\rangle$$

$$D_{ij} = \langle\phi_i| -\frac{1}{2}\Delta + v_{\text{eff}}|\phi_j\rangle - \langle\widetilde{\phi}_i| -\frac{1}{2}\Delta + \widetilde{v}_{\text{eff}}|\widetilde{\phi}_j\rangle$$

The all-electron and pseudo eigenvalue spectrum is identical, all-electron scattering properties are reproduced over a wide energy range.

$$\left(-\frac{1}{2}\Delta + v_{\text{eff}}\right)|\phi_i\rangle = \epsilon_i|\phi_i\rangle$$
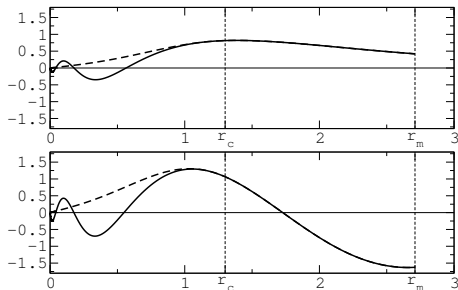
$$\left(-\frac{1}{2}\Delta + \widetilde{v}_{\text{eff}} + \sum_{kl}|\widetilde{p}_k\rangle D_{kl}\langle\widetilde{p}_l|\right)|\widetilde{\phi}_i\rangle = \epsilon_i\left(1 + \sum_{kl}|\widetilde{p}_k\rangle Q_{kl}\langle\widetilde{p}_l|\right)|\widetilde{\phi}_i\rangle$$

$$\left.\frac{\partial\widetilde{\phi}_l(r,\epsilon)}{\partial r}\frac{1}{\widetilde{\phi}_l(r,\epsilon)}\right|_{r=r_c} \approx \left.\frac{\partial\phi_l(r,\epsilon)}{\partial r}\frac{1}{\phi_l(r,\epsilon)}\right|_{r=r_c}$$

1st s-channel: ϵ_1
Mn $4s$ "bound" state

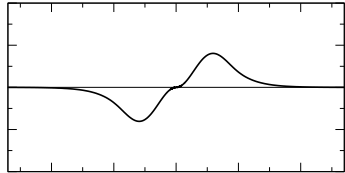

2nd s-channel: ϵ_2
Mn s "non-bound" state

Frozen core approximation:

$$v_{\text{eff}}[\rho_v] = v_H[\rho_v] + v_H[\rho_{Zc}] + v_{xc}[\rho_v + \rho_c] \qquad \rho_v(\mathbf{r}) = \sum_i a_i |\phi_i(\mathbf{r})|^2$$

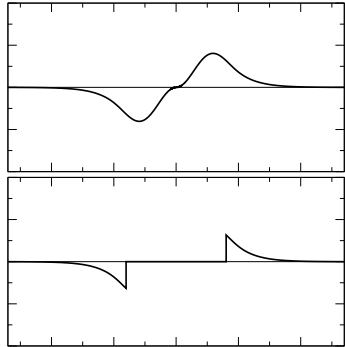$$\widetilde{v}_{\text{eff}}[\widetilde{\rho}_v] = v_H[\widetilde{\rho}_v] + v_H[\widetilde{\rho}_{Zc}] + v_{xc}[\widetilde{\rho}_v + \widetilde{\rho}_c] \qquad \widetilde{\rho}_v(\mathbf{r}) = \sum_i a_i |\widetilde{\phi}_i(\mathbf{r})|^2$$

$|\widetilde{\psi}_n\rangle$
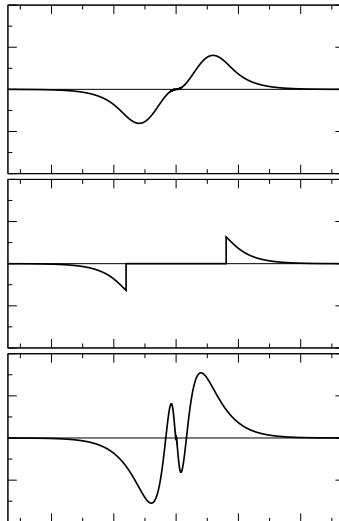
$|\widetilde{\psi}_n\rangle$

$|\widetilde{\psi}_n\rangle - \sum_i |\widetilde{\phi}_i\rangle\langle\widetilde{p}_i|\widetilde{\psi}_n\rangle$

$|\widetilde{\psi}_n\rangle$

$|\widetilde{\psi}_n\rangle - \sum_i |\widetilde{\phi}_i\rangle\langle\widetilde{p}_i|\widetilde{\psi}_n\rangle$

$|\widetilde{\psi}_n\rangle - \sum_i |\widetilde{\phi}_i\rangle\langle\widetilde{p}_i|\widetilde{\psi}_n\rangle + \sum_i |\phi_i\rangle\langle\widetilde{p}_i|\widetilde{\psi}_n\rangle$

- Character of wavefunction: $c_{lm\epsilon} = \langle \tilde{p}_{lm\epsilon} | \tilde{\psi}_n \rangle$

$$|\psi_n\rangle \quad = \quad |\tilde{\psi}_n\rangle \quad - \sum |\tilde{\phi}_{lm\epsilon}\rangle c_{lm\epsilon} + \sum |\phi_{lm\epsilon}\rangle c_{lm\epsilon}$$

AE = pseudo - pseudo-onsite + AE-onsite

- Same trick works for

  - Wavefunctions
  - Charge density

  - Kinetic energy
  - Exchange correlation energy
  - Hartree energy

The kinetic energy

- For instance, the kinetic energy is given by

$$E_{\mathrm{kin}} = \sum_n f_n \langle \psi_n | -\frac{1}{2}\Delta|\psi_n\rangle$$

- By inserting the transformation ($i = lm\epsilon$)

$$|\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle)\langle\tilde{p}_i|\tilde{\psi}_n\rangle$$

into E_{kin} one obtains: $E_{\mathrm{kin}} = \tilde{E} - \tilde{E}^1 + E^1$ (assuming completeness)

$$\underbrace{\sum_n f_n \langle\tilde{\psi}_n| -\frac{1}{2}\Delta|\tilde{\psi}_n\rangle}_{\tilde{E}} - \underbrace{\sum_{\mathrm{site}\ (i,j)} \rho_{ij}\langle\tilde{\phi}_i| -\frac{1}{2}\Delta|\tilde{\phi}_j\rangle}_{\tilde{E}^1} + \underbrace{\sum_{\mathrm{site}\ (i,j)} \rho_{ij}\langle\phi_i| -\frac{1}{2}\Delta|\phi_j\rangle}_{E^1}$$

- ρ_{ij} is an on-site density matrix:

$$\rho_{ij} = \sum_n f_n \langle\tilde{\psi}_n|\tilde{p}_i\rangle\langle\tilde{p}_j|\tilde{\psi}_n\rangle$$

- For any (quasi) local operator A there exists a PS operator

$$\tilde{A} = A + \sum_{ij} |\tilde{p}_i\rangle \left(\langle \phi_i | A | \phi_j \rangle - \langle \tilde{\phi}_i | A | \tilde{\phi}_j \rangle \right) \langle \tilde{p}_j |$$

so that

$$\langle \psi | A | \psi \rangle = \langle \widetilde{\psi} | \tilde{A} | \widetilde{\psi} \rangle$$

- For instance the PS operator that corresponds to the density operator $|\mathbf{r}\rangle\langle\mathbf{r}|$ is given by

$$|\mathbf{r}\rangle\langle\mathbf{r}| + \sum_{ij} |\tilde{p}_i\rangle \left(\langle \phi_i | \mathbf{r}\rangle\langle\mathbf{r} | \phi_j \rangle - \langle \tilde{\phi}_i | \mathbf{r}\rangle\langle\mathbf{r} | \tilde{\phi}_j \rangle \right) \langle \tilde{p}_j |$$

and the density

$$
\begin{aligned}
\langle \psi | \mathbf{r}\rangle\langle\mathbf{r} | \psi \rangle &= \langle \widetilde{\psi} | \mathbf{r}\rangle\langle\mathbf{r} | \widetilde{\psi} \rangle + \sum_{ij} \langle \widetilde{\psi} | \tilde{p}_i \rangle \left(\langle \phi_i | \mathbf{r}\rangle\langle\mathbf{r} | \phi_j \rangle - \langle \tilde{\phi}_i | \mathbf{r}\rangle\langle\mathbf{r} | \tilde{\phi}_j \rangle \right) \langle \tilde{p}_j | \widetilde{\psi} \rangle \\
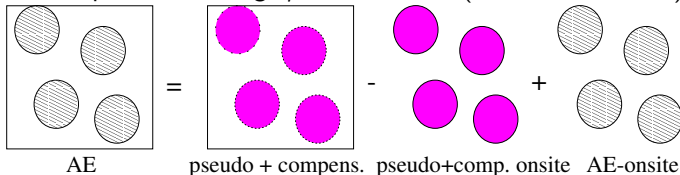&= \widetilde{\rho}(\mathbf{r}) - \widetilde{\rho}^1(\mathbf{r}) + \rho^1(\mathbf{r})
\end{aligned}
$$

- Non-local operators are more complicated

The Hartree energy

- The pseudo-wavefunctions do not have the same norm as the AE wavefunctions inside the spheres

- To deal with long range electrostatic interactions between spheres a soft compensation charge $\hat{\rho}$ is introduced (similar to FLAPW).

| AE | pseudo + compens. | pseudo+comp. onsite | AE-onsite |

- Hartree energy becomes: $E_H = \tilde{E} - \tilde{E}^1 + E^1$

$$E_H[\tilde{\rho} + \hat{\rho}] - \sum_{\text{sites}} E_H[\tilde{\rho}^1 + \hat{\rho}^1] + \sum_{\text{sites}} E_H[\rho^1]$$

$\tilde{\rho}^1$ one-center pseudo charge charge $\hat{\rho}^1$ one-center compensation

PAW energy functional

Total energy becomes a sum of three terms: $E = \tilde{E} + E^1 - \tilde{E}^1$

$$
\begin{aligned}
\tilde{E} =& \sum_n f_n \langle \tilde{\psi}_n | -\frac{1}{2}\Delta | \tilde{\psi}_n \rangle + E_{xc}[\tilde{\rho} + \hat{\rho} + \tilde{\rho}_c] + \\
& E_H[\tilde{\rho} + \hat{\rho}] + \int v_H[\tilde{\rho}_{Zc}]\left(\tilde{\rho}(\mathbf{r}) + \hat{\rho}(\mathbf{r})\right)\, d^3\mathbf{r} + \ U(\mathbf{R}, Z_{\text{ion}}) \\
\tilde{E}^1 =& \sum_{\text{sites}} \left\{ \sum_{(i,j)} \rho_{ij} \langle \tilde{\phi}_i | -\frac{1}{2}\Delta | \tilde{\phi}_j \rangle + \overline{E_{xc}[\tilde{\rho}^1 + \hat{\rho} + \tilde{\rho}_c]} + \right. \\
& \left. \overline{E_H[\tilde{\rho}^1 + \hat{\rho}]} + \int_{\Omega_r} v_H[\tilde{\rho}_{Zc}]\left(\tilde{\rho}^1(\mathbf{r}) + \hat{\rho}(\mathbf{r})\right)\, d^3\mathbf{r} \right\} \\
E^1 =& \sum_{\text{sites}} \left\{ \sum_{(i,j)} \rho_{ij} \langle \phi_i | -\frac{1}{2}\Delta | \phi_j \rangle + \overline{E_{xc}[\rho^1 + \rho_c]} + \right. \\
& \left. \overline{E_H[\rho^1]} + \int_{\Omega_r} v_H[\rho_{Zc}]\rho^1(\mathbf{r})\, d^3\mathbf{r} \right\}
\end{aligned}
$$

- $\tilde{E}$ is evaluated on a regular grid

  Kohn-Sham functional evaluated in a plane wave basis set

  with additional compensation charges to account for the incorrect norm of the pseudo-wavefunction (very similar to ultrasoft pseudopotentials).

  $\widetilde{\rho} = \sum_n f_n \widetilde{\psi}_n \widetilde{\psi}_n^*$ pseudo charge density

  $\hat{\rho}$ compensation charge

- E^1 and $\tilde{E}^1$ are evaluated on radial grids centered around each ion.

  Kohn-Sham energy evaluated for basis sets $\{\widetilde{\phi}_i\}$ and $\{\phi_i\}$

  these terms correct for the shape difference between the pseudo and AE wavefunctions.

- No cross-terms between plane wave part and radial grids exist.

- The pseudo wave functions $|\widetilde{\psi}_n\rangle$ (plane waves!) are the self-consistent solutions of

$$\left(-\frac{1}{2}\Delta+\widetilde{V}_{\text{eff}}+\sum_{ij}|\widetilde{p}_i\rangle(D_{ij}+...)\langle\widetilde{p}_j|\right)|\widetilde{\psi}_n\rangle = \epsilon_n\left(1+\sum_{ij}|\widetilde{p}_i\rangle Q_{ij}\langle\widetilde{p}_j|\right)|\widetilde{\psi}_n\rangle$$

$$D_{ij} = \langle\phi_i| -\frac{1}{2}\Delta + v^1_{\text{eff}}[\rho^1_v]|\phi_j\rangle - \langle\widetilde{\phi}_i| -\frac{1}{2}\Delta + \widetilde{v}^1_{\text{eff}}[\widetilde{\rho}^1_v]|\widetilde{\phi}_j\rangle$$
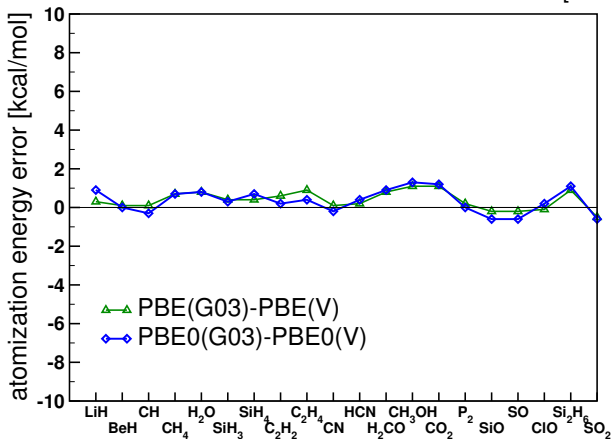
$$\rho^1_v(\mathbf{r}) = \sum_{ij}\rho_{ij}\langle\phi_i|\mathbf{r}\rangle\langle\mathbf{r}|\phi_j\rangle \qquad \widetilde{\rho}^1_v(\mathbf{r}) = \sum_{ij}\rho_{ij}\langle\widetilde{\phi}_i|\mathbf{r}\rangle\langle\mathbf{r}|\widetilde{\phi}_j\rangle$$

$$\rho_{ij} = \sum_n f_n\langle\widetilde{\psi}_n|\widetilde{p}_i\rangle\langle\widetilde{p}_j|\widetilde{\psi}_n\rangle$$

- If the partial waves form a complete basis within the PAW spheres, then the all-electron wave functions $|\psi_n\rangle$ are orthogonal to the core states!
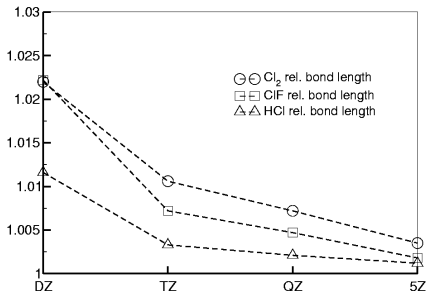
Accuracy

Subset of G2-1 test set: Deviation PAW w.r.t. GTO, in [kcal/mol].

$|\Delta E_{\mathrm{AE}}| < 1$ kcal/mol.

Accuracy

Relative PBE bond lengths of Cl_2, ClF, and HCl for various GTO basis sets specified with respect to plane-wave results:


aug-cc-pVXZ (X= D,T,Q,5)
N.B.: aug-cc-pV5Z basis set for Cl contains 200 functions!

$$|\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum_{lm\epsilon} \left(|\phi_{lm\epsilon}\rangle - |\phi_{lm\epsilon}\rangle\right) \langle\tilde{p}_{lm\epsilon}|\tilde{\psi}_n\rangle$$

- $|\tilde{\psi}_n\rangle$ is the variational quantity of the PAW method.
- The PAW method is often referred to as an all-electron method. Not in the sense that all electrons are treated explicitly, but in the sense that the valence electronic wave functions are kept orthogonal to the core states.

AE   pseudo + compens. pseudo+comp. onsite AE-onsite
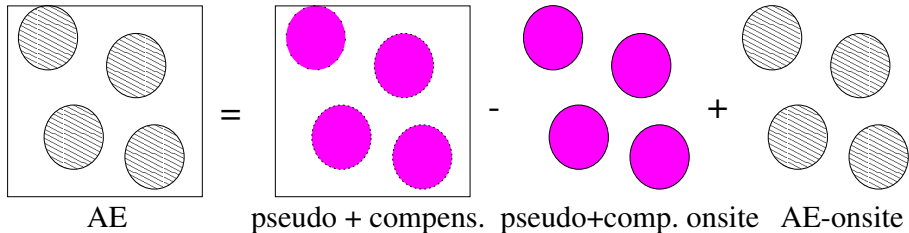
- This general scheme applies to all operators.

- Sometimes one may choose to include only parts of the PAW expressions.

  lazy: only implement plane wave part (GW, ...)
  efficient: physics of localized orbitals; only spheres (LDA+U, DMFT, ...,)